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Practical and versatile oxidation of alcohol using novel Na_2WO_4–H_2O_2 system under neutral conditions

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ABSTRACT

This paper presents a novel Na_2WO_4–H_2O_2 oxidation system. The oxidation of alcohol to ketone or aldehyde was carried out by using *N*,*N*-dimethylacetamide, hydrogen peroxide, and a catalytic amount of disodium tungstate dihydrate under neutral conditions. This method is very simple, practical for large-scale manufacturing, and applicable to a variety of substrates including an acid-sensitive substrate. Disodium tetraperoxotungstate dihydrate ($Na_2[W(O_2)_4]\cdot 2H_2O$) was isolated from a mixture of *N*,*N*-dimethylacetamide, hydrogen peroxide, and disodium tungstate dihydrate, and a proposal reaction mechanism is discussed in this paper.

1. Introduction

Oxidation of alcohols to aldehydes or ketones is one of the most important reactions in organic chemistry and various methods have been reported, for example, Jones oxidation,[1] Dess–Martin oxidation,[2] Oppenauer oxidation,[3] Swern oxidation,[4] and so on. However, these oxidations have not been often used in large-scale manufacturing because of inherent safety concerns and waste of byproducts.[5]

Recently, TEMPO catalyzed oxidation with NaClO[6] or $NaClO_2$[7] as primary oxidant, TPAP oxidation,[8] and tungsten peroxide, which is prepared from hydrogen peroxide (H_2O_2) and catalytic amount of sodium tungstate dihydrate ($Na_2WO_4\cdot 2H_2O$), catalyzed oxidation were reported as practical methodologies. Attention has been particularly drawn to a method of 'green' oxidation using tungsten peroxide.[9,10] However, the reactive pH range is limited to strong acidic conditions and it requires a commercially unavailable phase transfer catalyst.[9] We therefore aimed at developing a new mild and practical oxidation method that would use only commercially available reagents. Now a first example of tungsten peroxide oxidation of alcohol under neutral conditions is achieved, which is very simple, practical, and versatile method. The catalyst structure of $Na_2[W(O_2)_4]\cdot 2H_2O$ is clarified by single crystal X-ray analysis and the reaction mechanism is also discussed in this paper.

2. Results and discussion

2.1. Optimization of reaction conditions

The pH value of a tungsten peroxide aqueous solution, which was a mixture of aqueous H_2O_2 and a catalytic amount of $Na_2WO_4\cdot 2H_2O$, is 5.4. We first screened various solvents for the oxidation of 2-octanol to 2-octanone using this mixture (Table 1). The catalyst did not dissolve in many kinds of organic solvent, however, it dissolved in strong donor solvents such as 1,3-dimethyl-2-imidazolidinone (DMI), *N*,*N*-dimethylformamide (DMF), *N*-methylpyrrolidine (NMP), *N*,*N*-dimethylacetamide (DMA), and hexamethylphosphoramide (HMPA), and the oxidation of 2-octanol in such solvents gave 2-octanone in good yields. Although HMPA gave the best yield, it has a negative health impact.[11] Therefore, DMA and NMP were considered to be practical solvents for this oxidation. Next, we investigated the effects of the pH value of an aqueous solution of H_2O_2 and $Na_2WO_4\cdot 2H_2O$ on the oxidation of 2-octanol to 2-octanone in DMA (Table 2). Addition of NaOH decreased the yield of ketone even at pH 6.5 (entry 2). On the other hand, we found that addition of a phosphate salt accelerated the oxidation of 2-octanol to 2-octanone. Adjustment to pH 6.5 by adding $Na_2HPO_4\cdot 12H_2O$ maximized the yield (entry 3). To date, there has been no reported example of Na_2WO_4–H_2O_2 oxidation of alcohol under neutral condition. Under basic conditions,

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Table 1
Effect of solvent for oxidation of 2-octanol[a]

Entry	Solvent	Reaction temperature (°C)	2-Octanone[b] (%)
1	Acetonitrile	Reflux	7
2	Acetone	Reflux	0
3	Water	90	0
4	Methanol	Reflux	0
5	Dimethoxyethane	Reflux	0
6	DMI	90	40
7	DMF	90	50
8	NMP	90	73
9	DMA	90	74
10	HMPA	90	88

[a] The reaction was done using 2-octanol, H_2O_2, and $Na_2WO_4 \cdot 2H_2O$ in a 100:120:1 molar ratio for 3 h.
[b] Determined by GC analysis.

Table 2
Effects of additives and pH for oxidation of 2-octanol[a]

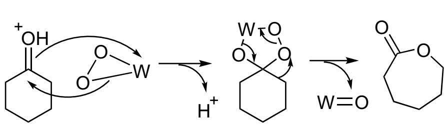
Entry	pH[b]	Additive	2-Octanone[c] (%)
1	5.4	—	74
2	6.5	NaOH	58
3	6.5	$Na_2HPO_4 \cdot 12H_2O$	94
4	8.3	Na_3PO_4	13
5	8.3	NaOH	0
6	10.2	NaOH, $Na_2HPO_4 \cdot 12H_2O$	0

[a] The reaction was done using 2-octanol, H_2O_2, and $Na_2WO_4 \cdot 2H_2O$ in a 100:120:1 molar ratio and additive (90 °C for 3 h in DMA).
[b] pH value of tungsten peroxide solution.
[c] Determined by GC analysis.

unproductive decomposition of H_2O_2 proceeded and the yield of ketone was unsatisfactory (entries 4–6).

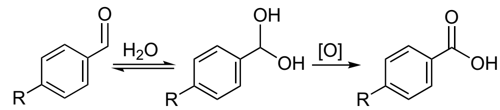
2.2. Scope and limitation

The substrate generality was investigated (Table 3). Oxidation of oleanolic acid gave the corresponding ketone in excellent yield (entry 1). Epoxidation by tungsten peroxide[12] at 12-ene did not occur in this oxidation. Oleanolic acid is a starting material of S-0139[13,14] and this oxidation has been applied to pilot manufacturing on a 22-kg scale.[15] 1-Phenylethanol was oxidized quantitatively (entry 2). The oxidation of 2-ethyl-1,3-hexanediol gave 2-ethyl-1-hydroxy-3-hexanone in good yield because the oxidation of secondary alcohol is faster than primary alcohol (entry 3). Although conventional $Na_2WO_4 \cdot 2H_2O$–H_2O_2 oxidation could not be applied to a substrate including THP protective group,[9] this method gave the corresponding ketone without decomposition of acid-sensitive pyranyl moiety (entry 4). Although the oxidation of cyclohexanol with excess H_2O_2 by a conventional method gave adipic acid with over oxidation, which is speculated to go through Bayer–Villiger oxidation,[10] in this oxidation over oxidation did not occur (entry 6). Bayer–Villiger oxidation by metal peroxo complexes requires protonation of ketone for an insertion of ketone into the metal–oxygen bond in acidic conditions (Eq. 1),[16] however, the insertion does not occur in neutral condition because ketone is not protonated.



(1)

In the oxidation of primary alcohols, benzyl alcohol and 4-methoxybenzyl alcohol can be oxidized to the corresponding aldehydes in excellent yield (entries 7 and 8). However, 4-nitrobenzyl alcohol gave *p*-nitrobenzaldehyde in only 20% yield (entry 9). Benzaldehyde which has electron-withdrawing group such as nitro group can be hydrated, therefore the oxidation to carboxylic acid is easy to proceed (Eq. 2). The oxidation of 2-ethyl-1-hexanol was also difficult to stop at the aldehyde stage (entry 10).



(2)

2.3. Reaction mechanism

The catalyst, which was isolated from a mixture of $Na_2WO_4 \cdot 2H_2O$–H_2O_2 in DMA solution, was determined to be disodium tetraperoxotungstate dihydrate $Na_2[W(O_2)_4] \cdot 2H_2O$ by a single crystal X-ray analysis (Fig. 1). Oxidation of 2-propanol using $Na_2[W(O_2)_4] \cdot 2H_2O$ was carried out in DMA and water. In water, unproductive decomposition proceeded, producing gas, and the yield of acetone was 0%. On the other hand, the oxidation in DMA gave acetone. To date, oxidation of alcohols using $Na_2[W(O_2)_4] \cdot 2H_2O$ has not been reported. Catalysts for conventional oxidations were diperoxo species.[9,10,17–19] Diperoxo species were prepared from a strong acidic solution.[20–23] According to conventional report, diperoxotungstate complexes have H_2O molecule as a ligand, and a ligand exchange of H_2O/alcohol occurs for a coordination of alcohol to tungsten.[9] This ligand exchange seemed to be a key step for the oxidation. However, $Na_2[W(O_2)_4]$ does not have H_2O ligand and the ligand exchange cannot be undergone. We estimate that this reaction mechanism is totally different from conventional oxidations.

According to previous report, $Na_2[W(O_2)_4]$ was very unstable for heat and gave almost 2 mol of singlet oxygen on thermal decomposition.[24] However, it was not deactivated by heat in the course of reaction. We investigated the exothermic onset temperature of $Na_2[W(O_2)_4]$ solution with DSC. Aqueous solution of $Na_2[W(O_2)_4]$ was decomposed even at 25 °C, however, the exothermic onset temperature of $Na_2[W(O_2)_4]$ in DMA was over 105 °C. We estimate that DMA solvent coordinates to tungsten and this coordination stabilizes the catalyst. In actuary it is known that amide compound can coordinate to tungsten.[25] So we propose a reaction mechanism described in Scheme 1. Na_2WO_4 (**1**) and H_2O_2 gives $Na_2[W(O_2)_4]$ (**2**). Although thermal cleavage of W–O bond occurs, coordination of DMA stabilizes catalyst **3**. Without DMA, **2** is decomposed to 2 mol of oxygen and 1 mol of **1** easily. Next, the ligand exchange of DMA/alcohol is undergone, the alkoxide ligand in **4** is dehydrogenated by hydroperoxo ligand, and finally ketone is produced. We think that the coordination is a key step for this oxidation. The yield for oxidation of 2-octanol to 2-octanone in HMPA, DMA, NMP, and DMF (Table 1) followed an order of Gutmann's donor number.[26] From this result, we think that the stability of catalyst is relied on the donicity of solvent, and the yield of ketone seems to be increased.

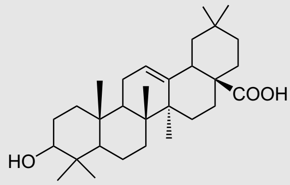
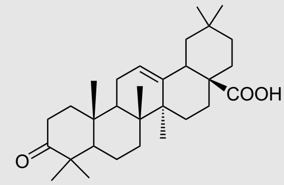
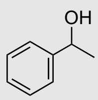
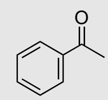
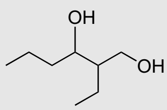
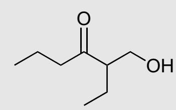
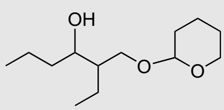
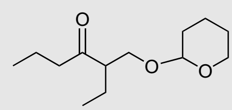
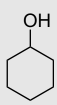
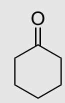
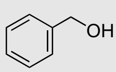
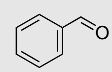
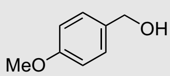
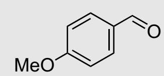
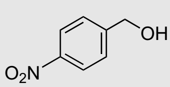
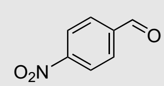
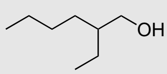
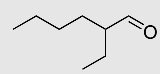
2.4. Caution of safety on large-scale synthesis

When this oxidation has been applied to pilot manufacturing of S-0139,[15] the cold mixture of H_2O_2, $Na_2WO_4 \cdot 2H_2O$, and $Na_2HPO_4 \cdot 12H_2O$ has been added dropwise into a 90 °C DMA solution of oleanolic acid for 1 h. Although $Na_2[W(O_2)_4]$ is stabilized in DMA, the reaction temperature is close to decomposition temperature of $Na_2[W(O_2)_4]$/DMA. Adiabatic temperature rise by reaction heat is possible to attain the decomposition temperature. However, the dropwise addition of the mixture of oxidant can control the reaction rate and heat, and then safety can be ensured.

3. Conclusion

The first successful $Na_2WO_4 \cdot 2H_2O$–H_2O_2 oxidation under neutral conditions was achieved by using $Na_2HPO_4 \cdot 12H_2O$ and an

Table 3
Oxidation of several alcohols[a]

Entry	Substrate	H_2O_2 (equiv)	Reaction time (h)	Product	Yield of ketone (%)
1		1.2	4		91[b]
2		1.2	1		>99[c]
3		1.2	2		74[d]
4		1.2	4		86[d]
5		1.2	4		98[e]
6		4.4	10		96[e]
7		1.1	1		90[c]
8		1.1	1		95[c]
9		1.1	4		20[c,f]
10		1.1	4		50[e,g]

[a] 35% H_2O_2, 1 mol % $Na_2WO_4 \cdot 2H_2O$, and 4 mol % $Na_2HPO_4 \cdot 12H_2O$ in DMA at 90 °C. Concentration of substrate was 0.2 M.
[b] Isolated by crystallization.
[c] Determined by HPLC analysis.
[d] Isolated by silica gel column chromatography.
[e] Determined by GC analysis.
[f] 4-Nitrobenzyl alcohol was recovered in 45% and *p*-nitrobenzoic acid was yielded in 35%, which were determined by HPLC.
[g] 2-Ethyl-1-hexanol was recovered in 33%, which was determined by GC.

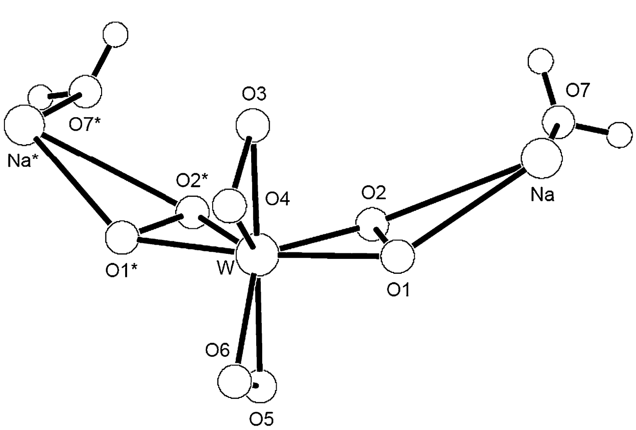


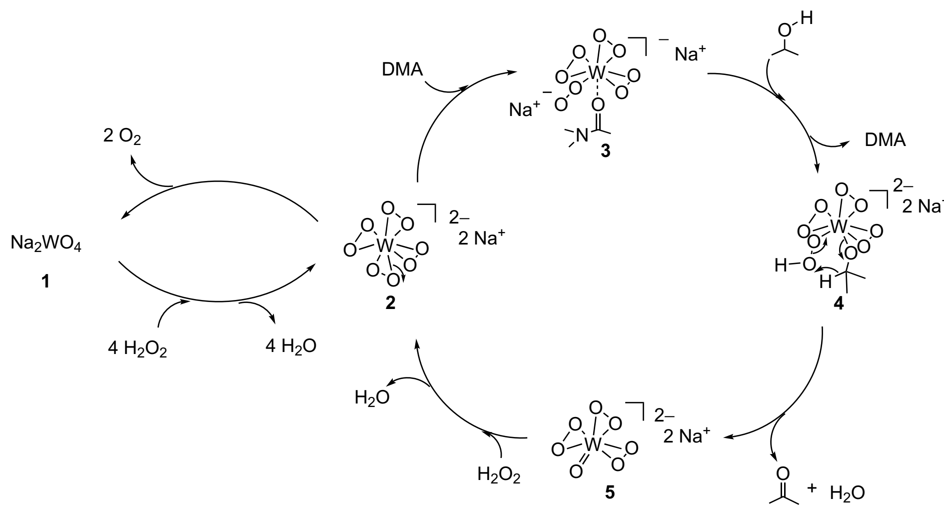
Figure 1. Single crystal X-ray structure of sodium tetraperoxotungstate.

amide solvent such as DMA. This method is very simple and versatile. The neutral conditions make it applicable to acid-sensitive substrates. This method was successfully applied to the oxidation of oleanolic acid on a 22-kg scale, which is the first step of S-0139 synthesis. We conclude that this alcohol oxidation method is practical for large-scale manufacturing. Reaction species was determined to be $Na_2[W(O_2)_4] \cdot 2H_2O$ by X-ray analysis. Although $Na_2[W(O_2)_4] \cdot 2H_2O$ aqueous solution is unstable for heat, it was stabilized in strong donor solvent and a novel oxidation using this catalyst was achieved.

4. Experimental section

4.1. General

^1H and ^{13}C NMR spectra were measured on a Varian Unity Inova 600. High-resolution mass spectra were recorded on JEOL JMS-SX/SX102A. Gas chromatographic (GC) analysis was carried out using



Scheme 1. Proposed reaction mechanism using tetraperoxotungstate.

HP 6780. High performance liquid chromatographic (HPLC) analysis was carried out using Shimadzu LC-2010HT. Sodium tungstate dihydrate and *N*,*N*-dimethylacetamide were obtained from Kanto Kagaku Co., Ltd. Hydrogen peroxide (35%), disodium phosphate dodecahydrate, 2-octanol, 1-phenylethanol, 2-ethyl-3-hydroxy-1-hexanol, cyclohexanol, benzyl alcohol, 4-methoxybenzyl alcohol, and 2-ethyl-1-hexanol were obtained from Wako Pure Chemical Industry. Oleanolic acid was obtained from Sichuan ShiFang Xihua Pharma raw material factory. 4-Nitrobenzyl alcohol was obtained from Across. Oxidation of 1-phenylethanol, cyclohexanol, benzyl alcohol, 4-methoxybenzyl alcohol, and 4-nitrobenzyl alcohol were run under conditions similar to the general procedure, and these yields were determined by HPLC or GC. 2-Octanone, acetophenone, cyclohexanone, benzaldehyde, benzoic acid, 4-methoxybenzaldehyde, *p*-nitrobenzaldehyde, *p*-nitrobenzoic acid, 2-ethyl-1-hexanal, and 2-ethyl-hexanoic acid were identified by NMR compared with authentic sample.

4.2. Caution of preparation of oxidant

Dissolution of $Na_2WO_4{\cdot}2H_2O$ into 30% H_2O_2 causes exothermic heat. Aqueous solution of $Na_2WO_4{\cdot}2H_2O$ and H_2O_2 is easy to be decomposed above 23 °C, therefore it should be prepared in the ice bath.

4.3. Typical procedure for optimizing reaction conditions (general procedure)

A solution of 1.0 g (7.68 mmol) of 2-octanol in 18 mL of DMA was heated to 90 °C, and a cold mixture of 1.05 g (9.36 mmol) of 30% H_2O_2, 121 mg (0.34 mmol) of $Na_2HPO_4{\cdot}12H_2O$, and 25 mg (0.076 mmol) of $Na_2WO_4{\cdot}2H_2O$ was added dropwise. Stirring of the reaction mixture was continued for further 3 h. The yield of 2-octanone was determined by GC. GC (FID): column, DB-WAX 0.53 mm×30 m, 1.0 μm (J&W Scientific); carrier gas, helium 1.0 mL/min; column temperature, 110 °C, 10 min; final temperature, 200 °C; progress rate, 30 °C/min; injection temperature, 250 °C; detector temperature, 250 °C; split ratio, 25:1; t_R of 2-octanol, 7.0 min; t_R of 2-octanone, 5.0 min.

4.4. Oxidation of oleanolic acid

A solution of 4.58 g (10.0 mmol) of oleanolic acid in 23 mL of DMA was heated to 90 °C, and a cold mixture of 1.18 g (12.0 mmol) of 35% H_2O_2, 144 mg (0.4 mmol) of $Na_2HPO_4{\cdot}12H_2O$, and 33 mg (0.1 mmol) of $Na_2WO_4{\cdot}2H_2O$ was added dropwise. The mixture was stirred at 90 °C for 4 h, and then 50 mL of toluene and 50 g of 5% brine including Na_2SO_3 were added to the reaction mixture. The organic layer was separated and washed with 5% brine. The organic layer was separated, the resultant was concentrated under reduced pressure at 40 °C, and acetonitrile solution (25 mL of acetonitrile, 5 mL of water) was added to obtain white crystals. By this procedure, 4.12 g (9.0 mmol) of 3-oxoolean-12-ene-28-oic acid was obtained.[13]

4.5. Oxidation of 2-ethyl-1,3-hexanediol

A solution of 7.30 g (50.00 mmol) of 2-ethyl-1,3-hexanediol in 100 mL of DMA was heated to 90 °C, and a cold mixture of 5.90 g (60 mmol) of 35% H_2O_2, 0.72 g (2 mmol) of $Na_2HPO_4{\cdot}12H_2O$, and 0.17 g (0.5 mmol) of $Na_2WO_4{\cdot}2H_2O$ was added dropwise. After the reaction was continued at 90 °C for 4 h, 100 mL of toluene and 100 g of 10% brine including Na_2SO_3 were added to the reaction mixture. The organic layer was separated and washed with 10% brine. The aqueous layer was extracted with 100 mL of toluene. The organic layers were combined and condensed under reduced pressure at 40 °C. The residue (22.7 g) was purified by silica gel column chromatography (200 g of SiO_2; 70–230 mesh ASTM made by Merck, hexane/ethyl acetate=6:4 as an eluent). By this procedure, 5.33 g (36.9 mmol) of 2-ethyl-1-hydroxy-3-hexanone was obtained.[9]

4.6. Oxidation of 6-(tetrahydro-2-pyranyloxy)-5-ethyl-4-hexanol

A solution of 11.5 g (50 mmol) of 6-(tetrahydro-2-pyranyloxy)-5-ethyl-4-hexanol in 100 mL of DMA was heated to 90 °C, and a cold mixture of 5.90 g (60 mmol) of 35% H_2O_2, 0.72 g (2 mmol) of $Na_2HPO_4{\cdot}12H_2O$, and 0.17 g (0.5 mmol) of $Na_2WO_4{\cdot}2H_2O$ was added dropwise. After the reaction was continued at 90 °C for 4 h, 100 mL of toluene and 100 g of 10% brine including Na_2SO_3 were added to the reaction mixture. The organic layer was separated and washed with 10% brine. The aqueous layer was extracted with 100 mL of toluene. The organic layers were combined and condensed under reduced pressure at 40 °C. The residue (11.4 g) was purified by silica gel column chromatography (300 g of SiO_2; 70–230 mesh ASTM made by Merck, hexane as an eluent). By this procedure, 9.80 g (43 mmol) of 6-(tetrahydro-2-pyranyloxy)-5-ethyl-4-hexanone with diastereomer mixture was obtained. ^{1}H NMR (600 MHz, $CDCl_3$, δ) 0.81–0.90 (m, 6H), 1.35–1.74 (m, 10H), 2.32–2.52 (m, 2H), 2.66–2.78 (m, 1H), 3.32–3.50 (m, 2H), 3.64–3.86

(m, 2H), 4.44–4.55 (tt, 1H). ^{13}C NMR (150 MHz, $CDCl_3$, δ) 11.35, 11.43, 13.47, 13.50, 16.17, 16.91, 18.68, 18.97, 20.90, 20.97, 24.88, 24.97, 29.97, 30.05, 43.812, 44.16, 52.46, 52.72, 60.72, 61.24, 67.27, 67.52, 97.29, 98.20, 212.21, 212.94. HRMS (FAB$^+$) calcd for $C_{13}H_{25}O_3$: ($[M+H]^+$), 229.1804; found (m/z): 229.1797.

4.7. Oxidation of 2-ethyl-1-hexanol

A solution of 3.26 g (25.0 mmol) of 2-ethyl-1-hexanol in 50 mL of DMA was heated to 90 °C, and a cold mixture of 2.78 g (27.4 mmol) of 35% H_2O_2, 0.36 g (1.0 mmol) of $Na_2HPO_4\cdot 12H_2O$, and 82.5 mg (0.25 mmol) of $Na_2WO_4\cdot 2H_2O$ was added dropwise. The reaction was continued at 90 °C for 4 h. The yield of 2-ethyl-1-hexanal was determined by GC. After the reaction 50 mL of toluene and 50 g of 10% brine including Na_2SO_3 were added to the reaction mixture. The organic layer was separated and washed with 10% brine. The aqueous layer was extracted with 50 mL of toluene. The organic layers were combined and condensed under reduced pressure at 40 °C. Into the residue, 30 g of 10% disodium carbonate solution and 30 mL of toluene were added and the aqueous layer was separated. Into the aqueous layer 62% sulfulic acid and 50 mL of toluene were added. The organic layer was separated and condensed under reduced pressure at 40 °C. The residue (1.08 g) was identified by NMR compared with authentic 2-ethyl-hexanoic acid. GC condition (FID): column, DB-WAX 0.25 mm×30 m, 0.25 µm; carrier gas, helium 1.0 mL/min; column temperature, 55 °C, 10 min; final temperature, 95 °C, 20 min; progress rate, 10 °C/min; injection temperature, 200 °C; detector temperature, 250 °C; split ratio, 5:1; t_R of 2-ethyl-1-hexanol, 16.3 min; t_R of 2-ethyl-1-hexanal, 5.6 min.

4.8. Preparation of $Na_2[W(O_2)_4]\cdot 2H_2O$

A solution of 2.15 g (6.52 mmol) of $Na_2WO_4\cdot 2H_2O$ and 18.0 g (158.8 mmol) of 30% H_2O_2 was added into 80 mL of DMA at room temperature, followed by stirring for a few minutes. Yellow crystals of $Na_2W(O_2)_4\cdot 2H_2O$ were obtained by filtration (2.07 g, 5.95 mmol). Single crystal of $Na_2[W(O_2)_4]\cdot 2H_2O$ was obtained from a solution of 107.72 mg (0.33 mmol) of $Na_2WO_4\cdot 2H_2O$, 0.76 g (7.71 mmol) of 35% H_2O_2, and 7 mL of DMA, which were left in a refrigerator (5 °C) for 2 days. The structure was determined by X-ray analysis.

4.9. Oxidation of 2-propanol using $Na_2[W(O_2)_4]\cdot 2H_2O$

Into 30 mL of DMA or water, 70.2 mg (1.16 mmol) of 2-propanol and 101.6 mg (0.29 mmol) of $Na_2[W(O_2)_4]\cdot 2H_2O$ were dissolved. The solution was heated to 65 °C and stirred for 2 h. On using DMA, generation of acetone was detected by GC (yield: 24%). GC (FID): column, DB-1 0.25 mm×30 m, 1.0 µm (J&W Scientific); carrier gas, helium 1.0 mL/min; column temperature, 35 °C, 5 min; final temperature, 100 °C; progress rate, 15 °C/min; injection temperature, 200 °C; detector temperature, 250 °C; split ratio, 20:1; t_R of acetone, 3.0 min; t_R of 2-propanol, 3.2 min.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.10.056.

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